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A SHORT NOTE ON LIGAND FIELD THEORY OF THE MAGNETIC ANISOTROPY AND SUSCEPTIBILITY OF Fe^{2+} TUTTON SALTS

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Investigations on the magnetic susceptibility and anisotropy of $Fe(NH_4SO_4)_2$, $6H_2O$ (Bose *et al.*, 1961) by Pryce's method shows a 20% reduction of the spin-orbit coupling owing to covalency effects. We have therefore, applied here the more reasonable and general method of molecular orbitals (Van-Vleck 1932, Stevens 1953, and Bose *et al.*, 1960) assuming that the covalency overlap is anisotropic.

The theoretical calculations of principal ionic susceptibilities of Fe^{2+} are made and compared with the experimental data on anisotropy and mean susceptibility for the salt $Fe(KSO_4)_2$, $6H_2O$ (Table I) which is isomorphous to the ammonium double salt previously investigated. It is assumed here as in the previous case that the ligand field has a small tetragonal component superposed on the predominant cubic part.

As no paramagnetic resonance data for Fe^{2+} Tutton salts is available, we compare the g—values of $Fe(KSO_4)_2$, $6H_2O$ with those of Tinkham's (1955) on FeF_2 diluted with ZnF_2. Since the crystalline fields in FeF_2 is truely orthorhombic the g-values are somewhat different in magnitude from that in Tutton salts but the order of magnitudes are comparable within the limits of approximations involved.

In the case of $Fe(NH_4SO_4)_2$, $6H_2O$, the tetragonal field coefficient Δ increases with temperature from a value of 270 cm^{-1} at 20°K to 650^{-1} cm. at 300°K. In the case of $Fe(KSO_4)_2$, $6H_2O$, Δ changes from 240^{-1} cm at 90°K to 640 cm^{-1} at 300°K. Thus we see that the order of the anisotropic field and also their variations with temperature are almost the same in the two cases. The increase in Δ with temperature is due to thermal expansion or relaxation effects in the salts. In the case of $Fe(NH_4SO_4)_2$, $6H_2O$ the spin—orbit coupling coefficient has been decreased by 20% from its free ion value of -103 cm^{-1} (Owen 1955, Bose *et. al.*,

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1961). In the case of $Fe(KSO_4)_2$, $6H_2O$ we find the spin orbit coupling $\zeta_{\parallel} = -$ -80 cm^{-1}, $\zeta_{\perp} = -83$ cm^{-1} instead of free ion value of -103 cm^{-1}. This indicates again almost the same overlap between the 3d Fe^{2+} and s- and p---O^{2-} charge clouds, except that the overlap here has been taken as anisotropic.

The details of the work will be published shortly elsewhere.

TABLE I

$Fe(KSO_4)_2$, $6H_2O$.

$k_{\parallel} = 0.95$, $\zeta_{\parallel} = 0.80$ cm^{-1}

$k_{\perp} = -80$, $\zeta_{\perp} = -88$ cm^{-1}

Temp. °K	cm.$^{-1}$	p^2	$p_{\parallel}^2 - p_{\perp}$	g—values
300	640	28.57 (28.58)	10.31 (10.34)	..
220	416	28.13 (28.08)	12.87 (12.70)	..
90	240	26.00 (26.27)	22.10 (22.01)	$g = 8.48$ (8.97 ± .02) $g = 0$ (0.)

The values in the parenthesis in the 3rd and 4th column indicate the experimental results of Bose (1948). The g-values within parenthesis in the 5th column are Tinkham's (1955).

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REFERENCES

Bose, A., 1948, *Ind. J. Physics.* **22**, 483.

Bose, A. Chakravarti A. S. and Chatterjee R, 1961. *proc. Roy. Soc. A* **261**, 207.

Bose, A. Chakravarti A. S. and Chatterjee R, 1960, *Proc. Roy. Soc. A.* **255**, 145.

Owen, J., 1955, *Proc. Roy. Soc. A.* **227**, 193.

Stevens K. W. H. 1953, *Proc. Roy. Soc. A.* **219**, 542.

Tinkham M. 1955, *Proc. Roy. Soc. A.* **236**, 535.

Van-Vleck J. H. 1932, *Phys. Rev.* **41**, 208.